Zinc isotopes as novel tracers for waste from electroplating industries and for biochemical processes in estuaries

Daniel F. ARAÚJO[1-4], Geraldo R. BOAVENTURA[1], Elton DANTAS[1], Wilson MACHADO[2]; Sambasiva PATCHINEELAM[2], Ana Paula RODRIGUES[2], Marly BABINSKY[3], Izabel RUIZ[3], Jerome VIERS[4], Dominik WEISS[5]

1-Universidade de Brasília, Instituto de Geociências, danielunb.ferreira@gmail.com
2-Universidade Federal Fluminense, Departamento de Geoquímica, wmachado@geoq.uff.br
3- Universidade de São Paulo, Instituto de Geociências, babinski@usp.br
4- Géosciences Environnement Toulouse (GET), jerome.viers@get.obs-mip.fr
5- Imperial College London, Department of Earth Science and Engineering, d.weiss@imperial.ac.uk

Abstract

In this this work, the stable isotopic composition of Zn was determined in sediments samples and rocks collected at the Sepetiba Ba (Rio de Janeiro, Brazil), and in ore samples with the aim to identify sources and sinks of anthropogenic Zn. The zinc isotopic compositions in all estuary samples (sediments cores and surface and SPM) presented a large variation of δ^{66}Zn values (0.30 to 1.15‰). The core samples showed a significant correlation between isotopic composition (expressed using δ^{66}Zn) and enrichment factor (EF). A two-end member mixing with Zn derived from weathering and erosion of rocks as natural end member and from electroplating waste as anthropogenic end member can account for the observed isotopic variations. We find that the Zn isotopic signature of sediments in the bay is linked to the hydrodynamics and reflects the contaminants sinks. The stable isotope systematics of Zn can act as a reliable tracer of electroplating wastes in complex estuarine environment.

Keywords: Zinc stable isotopes, isotopic geochemistry, Sepetiba Bay, heavy metals.

1. Introduction

Mining and metallurgical industries activities are significant sources of pollution. During ore processing, large quantities of wastes are released, which can contaminate the environment inducing major risks to biota and human health (Kossof et al.2014). The Zn isotopes fractionate under anthropogenic process such as smelting and electroplating generating anthropogenic fingerprints isotopically distinct from natural isotopic compositions (Sivry et al., 2008). In this work, Zn isotopic signatures in sediment cores, rocks, suspended particulate matter (SPM) and ore samples were determined in order to identify the sources and sinks of anthropogenic Zn in Sepetiba Bay, Brazil.

2. Study area

Sepetiba bay is a 519 km^2 semi-enclosed salt-water body located 60 Km south of Rio de Janeiro City. The rivers and artificial channels that flow into the bay drain an extensive watershed of approximately 2.654 km^2, which includes agricultural, industrial and urban areas. In the 1960s, the electroplating plant (from the Ingá Mercantil company) started to operate. The electroplating wastes (estimated in about 600,000 tons, and containing about 200 tons of Cd and 50,000 tons of Zn) were disposed in an area of 40 m^2 adjacent to the mangrove creek that cross the Saco do Engenho area (fig.1). Rainfalls continuously leached the waste tailing to the creek which flow directly to the bay (Barcellos, 1991). In 1998 the company bankrupted and the industrial activities were ceased.

3. Materials and Methods

3.1 *Sampling, sample preparation and elemental analysis*

The sediment cores were collected in five representative points of Sepetiba Bay (fig.1). The core T1, located in Saco do Engenho, is the main point of contamination for Zn and other heavy metals due to the release of effluents by the electroplating plant. Granite rock samples were collected around a quarry located at north of the Saco do Engenho's mangrove. Three willemite ores from Vazante deposit were analyzed to represent the main mineral refined in the electroplating. Superficial sediments were collected in the mangroves and eleven suspedend particulate matter were collected along the bay. The samples were digested on a hot plate using a multiple-step acid procedure with HF, HNO_3, HCl and Teflon beakers. For major elements analsyis, the samples were digested by fusion with lithium metaborate. Elemental analysis were perfomed using ICP-OES. The Enrichment Factor (EF) was calculated normalizing the Zn/Al ratios of samples by the Zn/Al ratio of granite rock.

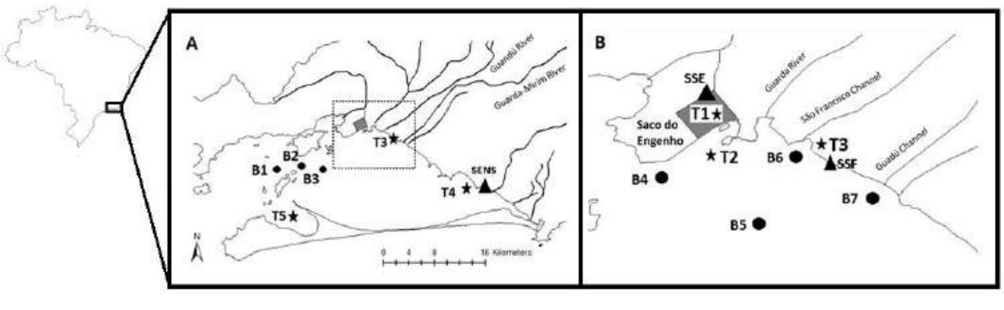

Fig.1. Map of the study area and location of sampling sites (stars to sediment cores; circles to suspended particulate matter and triangles to superficial sediments).

3.2 *Zn Isotopic Analysis*

Prior the isotopic analysis, the samples were purified by anion exchange chromatography using a modified protocol from that proposed by Maréchal et al. (1999). Zn isotopic ratios were measured using the Thermo Finnigan Neptune MC-ICP-MS at the Laboratório de Geocronologia of the University of Brasília and at Laboratorio do Centro de Pesquisas Geocronológicas (CPGeo) of the university of Sao Paulo.The $\delta^{66}Zn$ of the samples were then calculated as the deviation of the mass bias corrected Zn isotope ratio of the samples from the mean of the mass bias-corrected Zn isotopes rations of the bracketing standards.

$$\delta^{66}Zn(‰) = \left(\frac{^{66}Zn/\ ^{64}Zn_{sample}}{^{66}Zn/\ ^{64}Zn_{Standard}} - 1\right) 10^3 \quad \text{(eq.1)}$$

The external reproducibility obtained was 0.04‰ (n= 5, 2σ) for BHVO-2 and 0.06‰ (n=3, 2σ) for BCR-2. The average of external reproducibility of duplicate or triplicate analysis of unknowing samples were 0.04‰ (2σ).

4. Results and Discussions

The $\delta^{66}Zn$ determined on the sediment varied from 0.30 to 1.15‰. The T1 and T2 core, superficial sediments and SPM samples collected close to the mangrove impacted by the old tailing wastes (Saco do Engenho), presented high concentrations and an anomalous heavier isotopic composition ($\delta^{66}Zn$ values ranging from 0.68 to 1.15‰). The natural background considered corresponds the average of $\delta^{66}Zn$ values of the granite rock and the base profile samples of T3 core ($\delta^{66}Zn$ =0.28±0.12‰ (2σ), n=3). The SPM sampled in the inner bay and close the mouth of channels (B1, B2, B3, B4, B5, B6 and B7) presented a narrow range of $\delta^{66}Zn$ values (0.38 to 0.46‰, average 0.42± 0.06‰, 2σ). The sediment cores of Sepetiba bay presented good correlation between $\delta^{66}Zn$ values and the enrichment factor (fig.2). The sediments of T3, T4 and T5 cores align well between the isotopic compositions of granites and the sediments impacted by the electroplating wastes of Saco do Engenho indicating a conservative behavior of zinc isotopes in the bay. A mix model with two main sources: the electroplating wastes and natural background were developed using the equation 2:

$$f_{\%} = \left(\frac{\delta_{sample} - \delta_{natural}}{\delta_{anthropogenic} - \delta_{natural}}\right) * 100 \quad \text{(eq.2)}$$

Where $f_{\%}$ attends for the percentage of anthropogenic Zn; δ-anthropogenic and δ-natural for the isotopic compositions of the end members: electroplating wastes (0.86

±0.15‰, 2σ) and natural background (0.28 ± 0.12‰ (2σ)); δ-sample for isotopic compositions of each subsample of the profiles cores. The results point to a high content of anthropogenic Zn (more than 80%). The T3 and T5 cores present significant decreasing in the last years probably due to no more electroplating activities. On the other hand, the T4 core shows yet high contents of anthropogenic zinc derived from the wastes indicating preferential particle settling in this site.

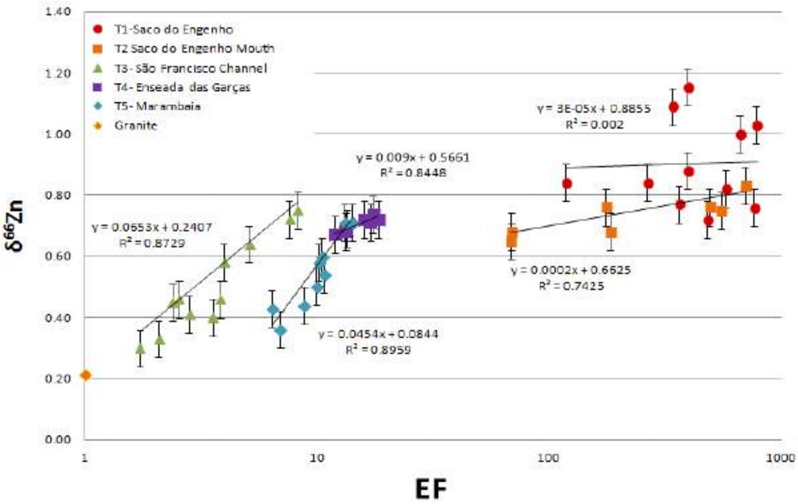

Fig.2. The plots between $\delta^{66}Zn$ against and enrichment factor of the core samples.

5. Conclusions

The Zn isotopic signatures are capable to trace the electroplating wastes in complex systems like Sepetiba bay, spatially and temporally. The isotopic signature of sediments in the bay is linked to the hydrodynamics and reflects the contaminants sinks.They can be used to assess the attenuation of electroplating wastes impacts in the next years as well identify possible new anthropogenic sources inputs. This work confirm the utility of Zn isotopes as tracers of contaminants in coastal areas.

6. References

Barcellos, C., Rezende, C.E., Pfeiffer, W.C., 1991. Zn and Cd production and pollution in a Brazilian coastal region. Marine Pollution Bulletin22, 558–561.

Kossoff, D., Dubbin, W. E., Alfredsson, M., Edwards, S. J., Macklin, M. G., and Hudson-Edwards, K. a. (2014). Mine tailings dams: Characteristics, failure, environmental impacts, and remediation. Applied Geochemistry, 51, 229–245.

Maréchal, C. N., Télouk, P., Albarède, F. (1999). Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. Chemical Geology, 156(1-4), 251-273.

Sivry, Y., Riotte, J., Sonke, J. E., Audry, S., Schäfer, J., Viers, J., Blanc, G., Freydier, R. and Dupré, B. (2008). Zn isotopes as tracers of anthropogenic pollution from Zn-ore smelters The Riou Mort–Lot River system. Chemical Geology, 255(3), 295-304.